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This study explored the importance of sediment resuspension on the distribution of hydrophobic organic contaminants (HOCs) in urban estuaries. The study consisted of three components: 1) a passive, in situ sampler, the polyethylene device (PED) was developed and tested; 2) the desorption rate of pyrene, a polycyclic aromatic hydrocarbon (PAH), was quantified from native Hudson River sediments; and 3) a field study was conducted to quantify the influence of sediment resuspension in the lower Hudson estuary on the distributions of pyrene and PCB #52.

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Anticipating Sediment Bed-to-Water Column Exchanges of Toxic Organic Compounds in Naval Harbors

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Abstract

This study explored the importance of sediment resuspension on the distribution of hydrophobic organic contaminants (HOCs) in urban estuaries. The study consisted of three components: 1) a passive, in situ sampler, the polyethylene device (PED) was developed and tested; 2) the desorption rate of pyrene, a polycyclic aromatic hydrocarbon (PAH), was quantified from native Hudson River sediments; and 3) a field study was conducted to quantify the influence of sediment resuspension in the lower Hudson estuary on the distributions of pyrene and PCB #52.

The polyethylene device (PED) is a small polyethylene sheet that is deployed in the aquatic environment to quantify water-column concentrations of dissolved HOCs. Like semipermeable membrane devices (SPMDs) and solid-phase microextraction (SPME), PEDs passively equilibrate with the chemical present in the system sampled, yielding information on the "truly" dissolved phase. PEDs provide for *in situ*, time-averaged measurements; they have fast equilibration times (on the order of days); and they enable relatively simple laboratory extraction and clean up before GC or GCMS analyses. Polyethylene-water partitioning constants and polyethylene diffusivity coefficients were measured in the laboratory over a range of temperatures so that dissolved concentrations from their field deployments could be calculated.

Observations of disequilibrium between HOCs (e.g., PAHs and PCBs) in sediment beds and the overlying waters indicate that the times for bed-water column transfers are important for understanding the fate of HOCs. Resuspended particles can play a significant role in the bed-water exchanges of such HOCs. For PAHs, like pyrene, these chemicals' strong affinity for black carbon, in addition to partitioning to the rest of the natural organic matter, makes the rate of desorption less certain. The desorption rate for pyrene from native

Hudson River sediment was measured in the laboratory and a diffusion rate constant (effective diffusivity/particle radius2) ranging from 1.0E-7 to 5.6E-7 s^{-1} was measured. The results were in good agreement with a physically- and chemically-based model for estimating effective diffusivity and the rate of desorption.

The elevated levels of PAHs and PCBs in the sediments of the lower Hudson Estuary, coupled with the tidally-driven sediment resuspension that occurs there, promote the transport of these HOCs to and from the overlying water column. PED-measured dissolved concentrations of pyrene and PCB #52 were quantified during both neap and spring tides during April and October field campaigns in order to assess the impact of increased sediment resuspension. The chemical potential in the sediments was found to be higher than that of the overlying waters for both pyrene and PCB #52. A comparison to other sources and sinks suggest that sediment resuspension is an important source. A one-box model was used to estimate the dissolved concentration within the estuary assuming steady state applied. This allowed for the validity of the model to be assessed and for missing sources or sinks to be examined. In April 1999 resuspended sediments appear to have served as a source of pyrene to the estuary, while during October 2000 the sediments and water were close to equilibrium suggesting a diminished source of pyrene to the overlying water. In contrast, mixing diagrams in April 1999 suggest that the resuspended sediments were serving as a sink, scavenging PCB #52. However, the sediment and water samples indicate that there was a driving force from the sediments to the water. A possible explanation for this observation may be the scavenging of PCB #52 by "cleaner" sediments throughout the estuary. In October 2000, as with pyrene, the sediments and water were more closely equilibrated with respect to PCB #52. These results show that sediment resuspension is important to the cycling of PAHs and PCBs in the lower Hudson Estuary.

Introduction

Once in the aquatic environment, the hydrophobic nature of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) causes them to preferentially sorb to the sediments (Karickhoff et al., 1979). Consequently, even after the input of these contaminants has ceased or diminished, the sediments can remain a source of pollutants to the surrounding water. Recent studies indicate that the sediments of urban bodies of water are a source of hydrophobic organic contaminants (HOCs) to the overlying water column (Chen, 1993; Achman et al., 1996; Flores, 1998; Petroni and Israelsson, 1998; Mitra et al., 1999). The significant resuspension events that occur in the lower Hudson Estuary (Hirschberg and Bokuniewicz, 1981; Geyer, 1995; Woodruff et al., 2001) may result in large fluxes of PAHs and PCBs to the surrounding waters. Recent studies in the Hudson (Achman et al., 1996; Adams, 2000) suggest that this is the case. It is important to improve our understanding of the extent to which sediment resuspension and subsequent chemical desorption play a role in the release of PAHs and PCBs to the water column so that we may improve our understanding of the mechanisms governing the fate of these chemicals in the environment. This improved understanding will aid environmental regulators and scientists in understanding the effects of these chemicals on the surrounding ecosystem and

organisms and assist for the selection of appropriately protective sediment quality criteria (U.S. EPA, 1993 and 1998).

The overall goal of this research was to further our understanding of the fate of PAHs and PCBs in the aquatic environment, specifically, the importance of sediment resuspension on the sediment bed-water column transport of HOCs in the lower Hudson Estuary. In order to accomplish this goal the following tasks were completed: 1) a passive, *in situ* sampler, a polyethylene device (PED), for measuring HOCs in the aquatic environment was developed; 2) the desorption rates of pyrene, a PAH, from native Hudson River sediments were measured, and 3) a field study was conducted to quantify the influence of sediment resuspension in the lower Hudson estuary an the distribution of pyrene and PCB #52 (2,2',5,5'-tetrachlorobiphenyl).

The suspension of contaminated particles is of particular concern as it allows for direct contact between solids carrying sorbed pollutants and the surrounding water. Several researchers have studied the importance of particle cycling on the fate of PAHs and PCBs in lakes (Baker and Eisenreich, 1989; Baker et al, 1991; Sanders et al., 1996) and estuaries (Zhou et al., 1996; Fernandes et al., 1997; Zhou et al., 1999). Depending on the difference in chemical potential between the sediments and water, particles may serve as a source or sink for HOCs in the surrounding waters.

Summary of Approach and Key Results

1. Development and Testing of the Polyethylene Device (PED)

A suite of laboratory tests were performed to determine the effectiveness of PEDs for quantifying dissolved concentrations of HOCs, to determine partition coefficients and their dependencies on temperature, and to assess equilibration times. These tests confirm that PEDs provide an effective means of quantifying the dissolved concentrations of HOCs at the low concentrations typical of the marine coastal environment. The equilibration timescale is on the order of days, which effectively integrates over short-timescale variability such as tidal oscillations. The large polyethylene-water partition coefficients for HOCs (see Table 1) were similar in magnitude to octanol-water partition coefficients. Such enrichment factors make the measurement of small concentrations of HOCs in water much less labor-intensive than the extraction of large volumes of water. Concentrations as low as 200 fM (e.g., PCB #52) were measured using PEDs.

Table 1. Polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) equilibrium partitioning coefficients between polyethylene and water @ 23°C[a]

Chemical	Log Kpew[b] PED & Water Extraction Exp.	Log Kpew[b] Water Sampling Experiment	Log Kow[c]	Source
PAHs				
Phenanthrene	4.3 ± 0.1	4.23 ± 0.02	4.5 ± 0.1	Mackay et al. (1992)
2-Methyl Phenanthrene	4.8 ± 0.2		5.2	Hansch et al. (1995)
Fluoranthene	4.9 ± 0.1		5.1 ± 0.2	Mackay et al. (1992)
Pyrene	5.0 ± 0.1	5.02 ± 0.03	5.0 ± 0.2	Mackay et al. (1992)
Benz(a)anthracene	5.7 ± 0.1		5.62 ± 0.02	Mackay et al. (1992)
d12-Benz(a)anthracene	5.7 ± 0.1			
Chrysene	5.7 ± 0.1		5.9 ± 0.1	Mackay et al. (1992)
Benzo(e)pyrene	6.2 ± 0.1		6.3 ± 0.2[d]	Mackay et al. (1992)
Perylene	6.5 ± 0.2		6.3	Sangster (1989)
PCBs				
2,4,5 TriCB (#29)	5.1 ± 0.1[e]		5.6	Hawker & Connell (1988)
2,2',5,5' TetraCB (#52)		5.4 ± 0.1	5.8	Hawker & Connell (1988)
2,3',4,6 TetraCB (#69)	5.6 ± 0.2[e]		6.0	Hawker & Connell (1988)

[a]Errors shown are ± 1 s.d.[b]log [(mol/kg$_{PE}$)/(mol/L$_W$)]. [c]log [(mol/L$_O$)/(mol/L$_W$)]. [d]The K_{OW} for benzo(a)pyrene is used for comparison as there were no experimental data available for benzo(e)pyrene. [e]These values were measured by Rainer Lohmann in the Gschwend Laboratory.

2. Quantifying the rate of desorption of pyrene from Hudson River sediments

In this study we examined pyrene, a PAH already present in the sediments, in order to estimate the desorption rates of pyrene from native Hudson estuary sediment. The use of native sediments allowed for the study of the effects of black carbon on PAH desorption. To our knowledge, this is the first study of the desorption of a PAH from native sediment. Sediment was collected with a box-corer from the lower Hudson estuary, and the fine silt fraction (38-88 □m) that predominates in this region's deposits was used in the desorption experiments. Sediment was added to 10 L of clean water in beakers and was maintained in suspension in beakers via stirring rods. Concentrations of desorbed pyrene were measured over time with time-gated, laser-induced fluorescence.

As reported by Gustafsson et al. (1997), the presence of black carbon significantly augmented the partition coefficient, significantly reducing the fraction of pyrene ultimately reaching the dissolved phase. The organic carbon content of the sediment was approximately 1% by weight, and the black carbon content was 0.2%. The effective K_d was found to be 53,000 ± 12,000 (L/kg), with an effective log K_{BC} of 6.8 (±0.4) estimated for the black carbon contribution. This value is higher than, but close to, the range observed in earlier measurements in Boston Harbor (Accardi-Dey and Gschwend, 2002). Despite the fact that between 66 and 98% of the pyrene is believed to have been desorbing

from black carbon, the retarded radial diffusion model of Wu and Gschwend allowed for the estimation of an effective diffusivity that fit experimental results.

The timescale for desorption was estimated using the radial diffusion model of Wu and Gschwend (1986, 1988), based on the estimated distribution coefficients and sediment properties. For relatively high suspended sediment concentrations of 300 mg/l typically found in the near-bottom waters, the timescale for 50% equilibration is 5-30 minutes, and for 90% equilibration is 4-20 hours. For 10 mg/l, typical of the near-surface waters, the 50% equilibration timescale is 8-40 hours and the 90% equilibration timescale is 3-10 days. This indicates that the near-bottom waters will typically reach equilibrium within the tidal timescale of sediment resuspension, whereas the near-surface waters may not reach equilibrium, particularly during high river-flow conditions when the residence time of the surface waters in the estuary may only be 1-3 days.
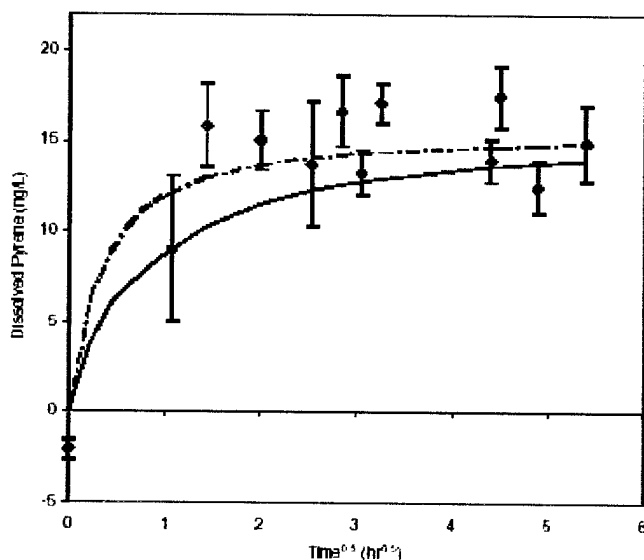

Figure 1. Dissolved pyrene (ng/L) (solid diamond) vs. time$^{0.5}$ at 25$\Box$C . The error bars are $\Box$1 s.d. When the first four experimental data points were fit, the resulting $Deff/a^2$ was 5.6E-7s^{-1} (dotted line). When only the first two data points were used to fit, the $Deff/a^2$ was 1.0E-7 s^{-1} (solid line).

3. Field investigation of influence of resuspension on the distribution of HOCs

Observations of water column concentrations of PAHs and PCBs were obtained using PEDs during two observation periods, in April 1999, during high river-flow conditions, and October 2000, during a low river-flow period. The water column observations were obtained along a 30-km segment of the estuary, between the Battery at the southern tip of Manhattan and Hastings, N.Y. This section of the estuary contains the lower-estuary turbidity-maximum zone (Geyer et al., 2000), where near-bottom suspended sediment concentrations reach 1,000 mg/l or more during spring tides. The PED-measured dissolved

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concentrations were sampled during both neap and spring tides in order to assess the impact of increased sediment resuspension. Dissolved concentrations were examined with respect to salinity, which was used as an index of conservative mixing. Sediment concentrations were used to predict the expected direction of chemical movement based on the concentration gradient between the sediments and the overlying water. The magnitudes of the predominant sources and sinks of pyrene and PCB #52 were estimated. Finally, the expected dissolved concentration of each chemical within the estuary was calculated with a simple, one-box model assuming steady state.

In the high river-flow conditions of April 1999, the sediments within the lower Hudson estuary provided for the input of pyrene into the overlying waters (Fig. 2). However, the sediments and water appear to have been more closely equilibrated during the low river-flow conditions of October 2000 (Fig. 3), resulting in a relatively small flux of pyrene from the sediments to the water column. This difference can potentially be explained by the difference in residence time between the high-flow and low-flow periods. When the residence time is short due to high river flow and enhanced estuarine transport, the desorption kinetics are not rapid enough to reach equilibrium, resulting in a gradient in concentration between the sediment and the water and a net flux from the sediment. During periods of longer residence time, the overlying water approaches equilibrium with the sediment, and the vertical flux is significantly reduced.
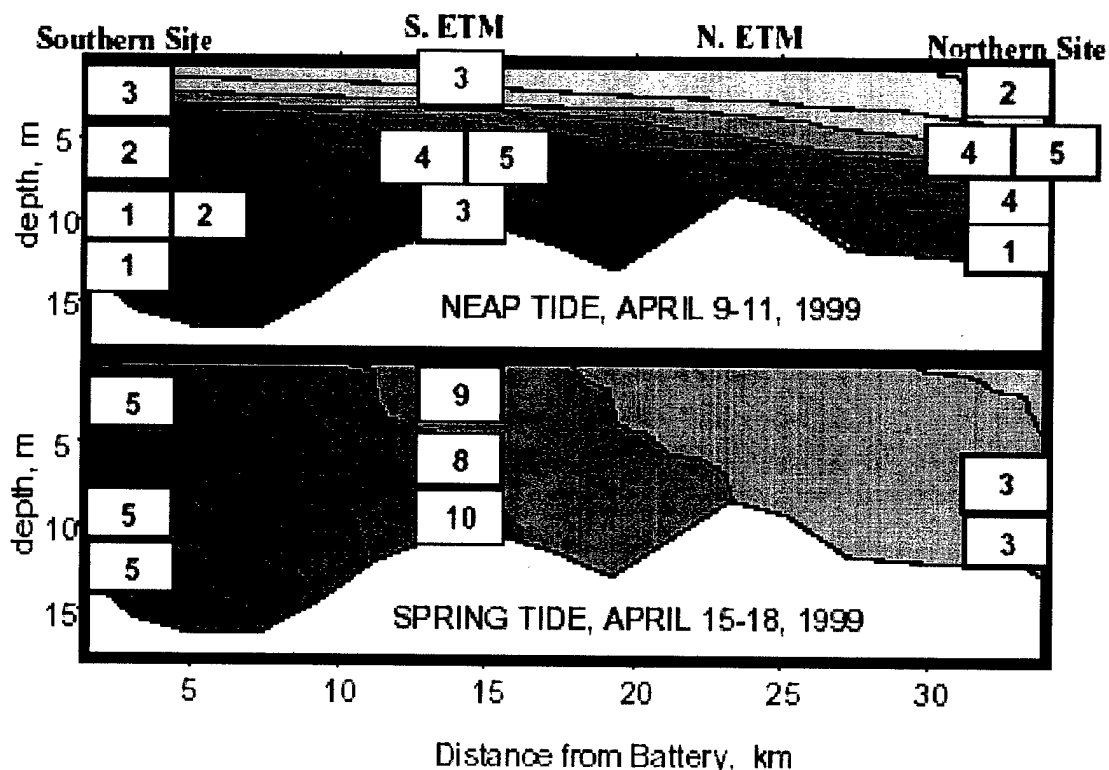

Figure 2. PED-measured dissolved pyrene concentration (ng/L) in the lower Hudson Estuary during neap tide (April 9-11, 1999) and spring tide (April 15-18, 1999). Contours

depict representative salinity gradients within the estuary during neap and spring tides with darker contours representing more saline water and the lighter contours depicting fresher water (Geyer et al., 1999).
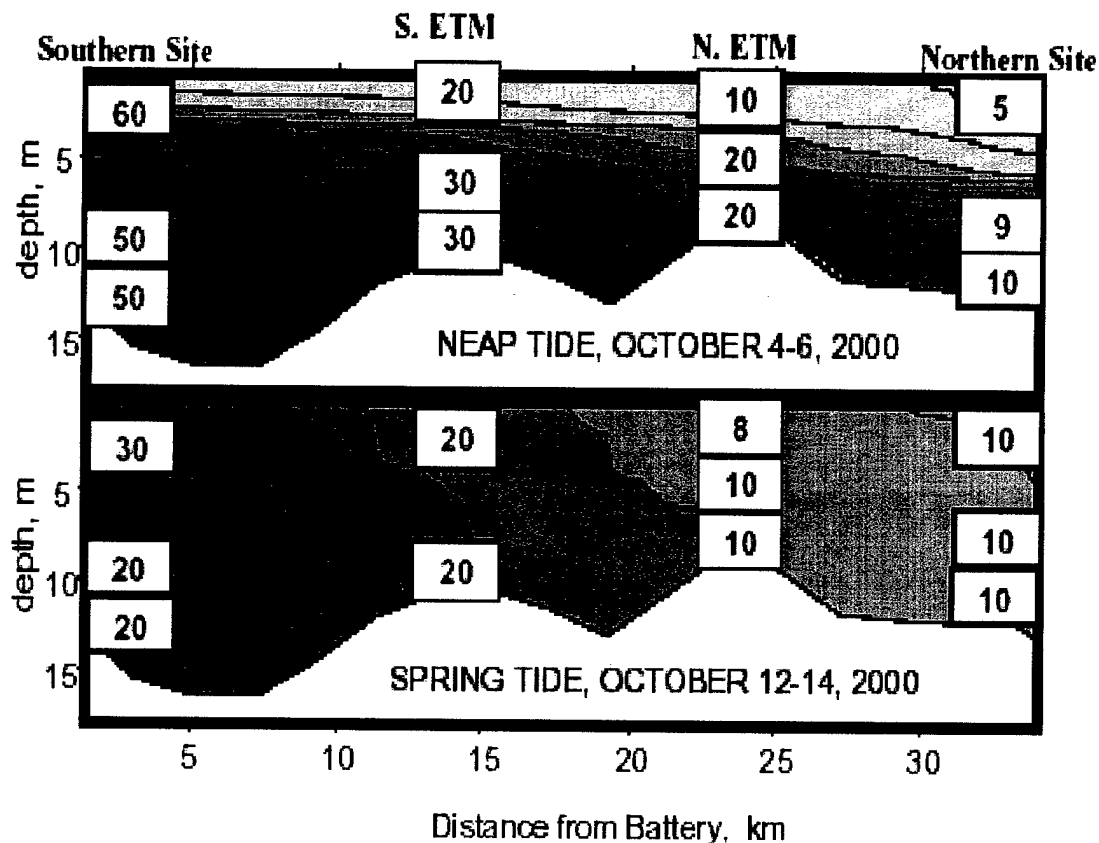

Figure 3. PED-measured dissolved pyrene concentration (ng/L) in the lower Hudson Estuary during neap tide (October 4-6, 2000) and spring tide (October 12-14, 2000). The upper-most PEDs are 2 m below the surface, and the deeper PEDs are 2 and 1 m from the river bottom. Contours depict representative salinity gradients within the estuary during neap and spring tides with darker contours representing more saline water and the lighter contours depicting fresher water (Geyer et al., 1999).

The PCB distributions indicate a different and possibly more complicated exchange process. During the high flow period, the water-column data suggest that the estuarine sediments functioned as a sink for PCB #52 (Fig. 4), whereas the sediment concentration data suggest that they should have been releasing PCB to the water column. One possible explanation for this observation is that the PCB was scavenged by cleaner sediments occurring elsewhere within the estuary. This hypothesis is supported by the geophysical data (Woodruff et al., 2000) that indicates significant heterogeneity of the sediment distribution within the estuary, which may also be associated with heterogeneity of the

contaminant concentrations. During low flow, the PCBs, like the pyrene, were close to equilibrium, and there was minor sediment-water exchange (Fig. 5).
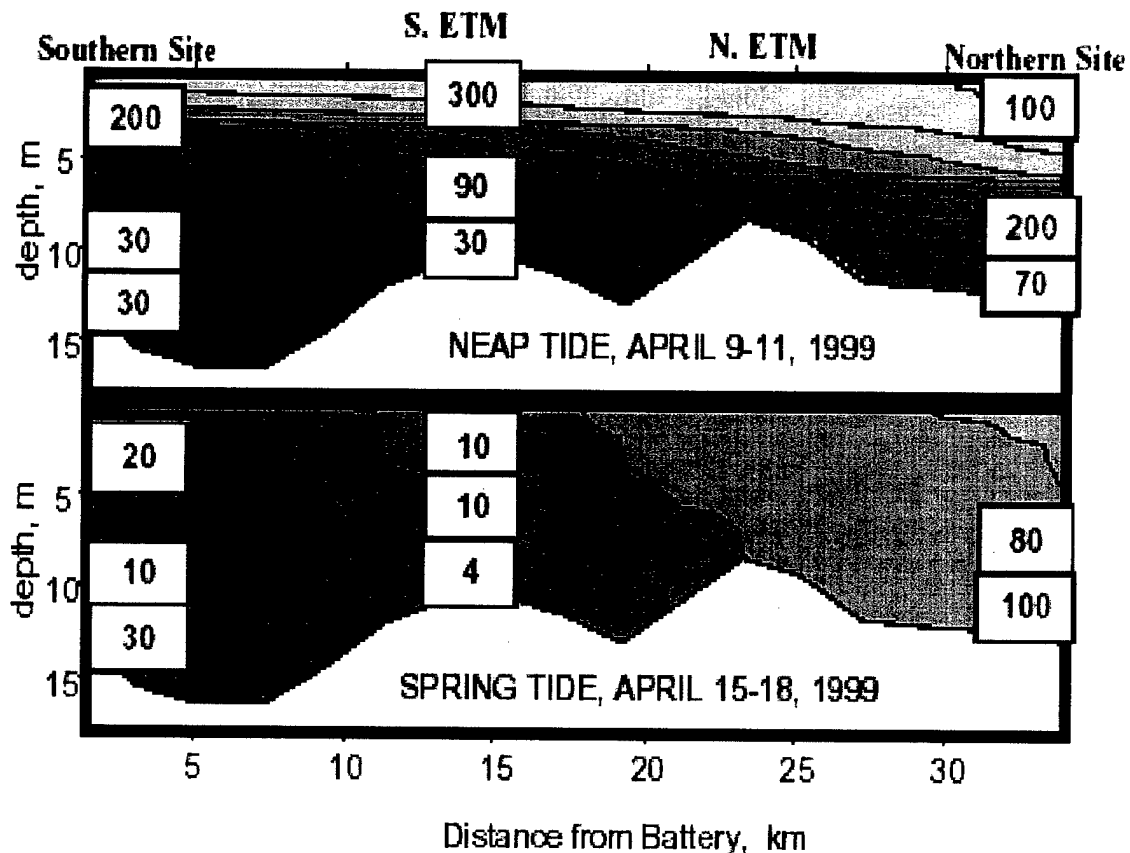

Figure 4. PED-measured dissolved PCB #52 concentration (pg/L) in the lower Hudson Estuary during neap tide (April 9-11, 1999) and spring tide (April 15-18, 1999). Contours depict representative salinity gradients within the estuary during neap and spring tides with darker contours representing more saline water and the lighter contours depicting fresher water (Geyer et al., 1999).
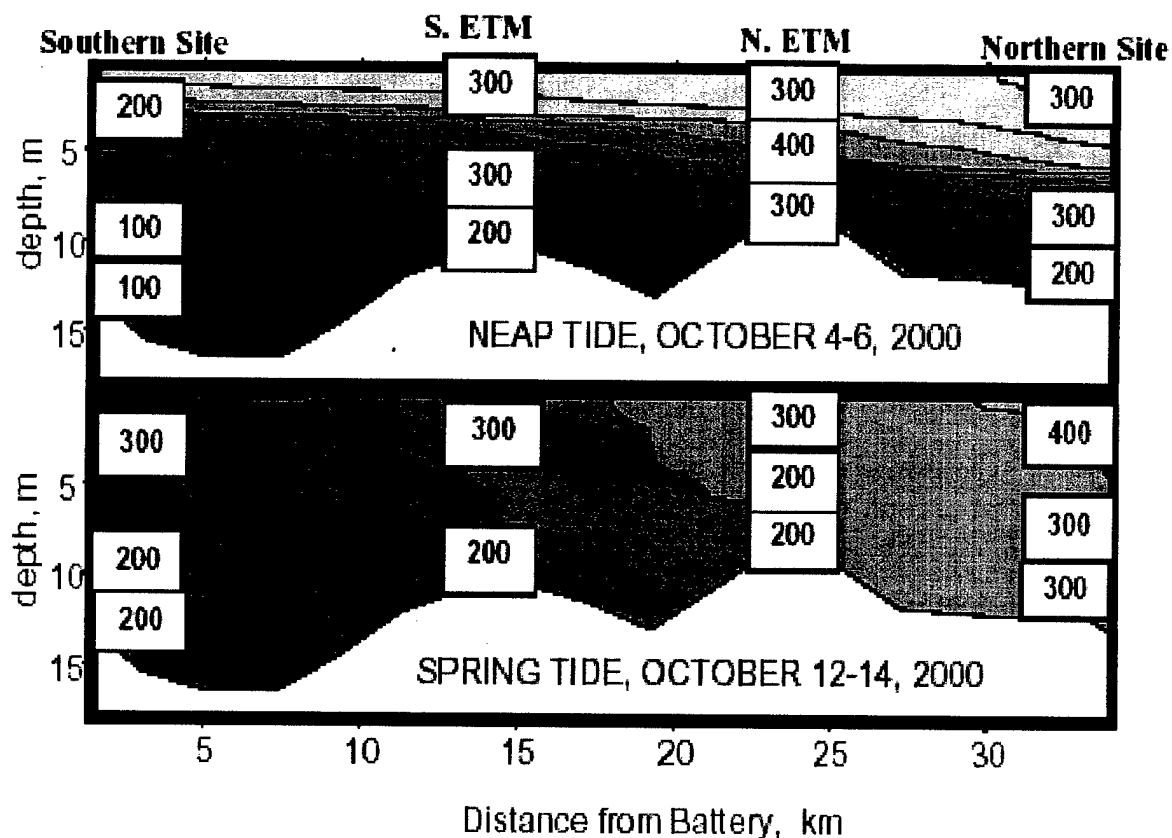
Figure 5. PED-measured dissolved PCB #52 (pg/L) in the lower Hudson Estuary during neap tide (October 4-6, 2000) and spring tide (October 12-14, 2000). The uppermost PEDs are 2 m below the surface, and the deeper PEDs are 2 and 1 m from the river bottom. Contours depict representative salinity gradients within the estuary during neap and spring tides with darker contours representing more saline water and the lighter contours depicting fresher water (Geyer et al., 1999).

Conclusions

Polyethylene devices (PEDs) provide a promising approach to quantifying the dissolved concentrations of organic contaminants in estuarine environments. Their ability to resolve low concentrations and integrate over tidal variations makes them effective tools for quantifying gradients of contaminant concentrations in energetic coastal and estuarine environments.

The sediment bed is a major reservoir of hydrophobic organic contaminants. The release of such contaminants to the water column can be significantly enhanced by resuspension,

particularly in an energetic and turbid estuary such as the Hudson River. However, high rates of resuspension do not necessarily result in large sediment-to-water fluxes. During periods of low river flow, when the estuarine residence time is long relative to the equilibration timescale of desorbing contaminants, there may be little net exchange between the bed and the water column, even with high concentrations of resuspended sediments. The flushing timescale of the estuary is thus a key variable for mediating the exchange between the sediments and the water column.

Publications

Adams, R.G. 2002 Polyethylene Devices and the Effects of Sediment Resuspension on the cycling of PAHs and PCBs in the lower Hudson Estuary. Ph.D. Thesis, MIT.

Geyer, W.R., J.D. Woodruff and P. Traykovski. 2001. Sediment transport and trapping in the Hudson River estuary. *Estuaries,* 24: 670-679.

Woodruff, J. D.; Geyer, W. R.; Sommerfield, C. K.; Driscoll, N. W. 2001. Seasonal variation of sediment deposition on the Hudson River Estuary. *Marine Geology, 179,* 105-119.

Adams, R. G. *Sediment-Water Exchange of Polycyclic Aromatic Hydrocarbons in the Lower Hudson Estuary*; Massachusetts Institute of Technology: Cambridge, 2000, pp 112.

Zhou, J. L.; Fileman, T. W.; Evans, S.; Donkin, P.; Readman, J. W.; Mantoura, R. F. C.; Rowland, S. 1999. The partition of fluoranthene and pyrene between suspended particles and dissolved phase in the Humber Estuary: a study of the controlling factors. *Sci. Total Environ., 243/244,* 305-321.

Mitra, S.; Dellapenna, T. M.; Dickhut, R. M. 1999. Polycyclic aromatic hydrocarbon distribution within lower Hudson River estuarine sediments: physical mixing vs. sediment geochemistry. *Estuar Coast Shelf S, 49,* 311-326.

Geyer, W. R.; Gschwend, P. M.; Adams, R. G. *Sediment-water column exchange of toxic organic compounds*; Office of Naval Research: Arlington, VA, 1999.

Flores, A. E. *Assessing the Fate of PAHs in the Boston Inner Harbor Using Semipermeable Membrane Devices (SPMDs)*; Massachusetts Institute of Technology: Cambridge, MA, 1998, pp 121.

Petroni, R. N.; Israelsson, P. H. *Mass Balance of 3D Model of PAHs in Boston's Inner Harbor*; Massachusetts Institute of Technology: Cambridge, MA, 1998, pp 224.

U.S.EPA "EPA's contaminated sediment management strategy.," U.S. EPA Office of Water, 1998.

N.O.A.A. "Sediment Toxicity in U.S. Coastal Waters," National Oceanic and Atmospheric Administration, Coastal Monitoring and Bioeffects Division, Office of Ocean Resources Conservation and Assessment, Coastal Ocean Program, 1998.

Fernandes, M. B.; Sicre, M.-A.; Boireau, A.; Tronczynski, J. 1997. Polyaromatic hydrocarbon (PAH) distribution in the Seine River and its estuary. *Mar. Pollut. Bull.*, *11*, 857-867.

Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. 1997. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.*, *31*, 203-209.

Achman, D. R.; Brownawell, B. J.; Zhang, L. 1996. Exchange of polychlorinated biphenyls between sediment and water in the Hudson River Estuary. *Estuaries*, *19*, 950-965.

Sanders, G.; Hamilton-Taylor, J.; Jones, K. C. 1996. PCB and PAH dynamics in a small rural lake. *Environ. Sci. Technol.*, *30*, 2958-2966.

Zhou, J. L.; Fileman, T. W.; Evans, S.; Donkin, P.; Fauzi, R.; Mantoura, C.; Rowland, S. J. 1996. Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary in Humber coastal zone. *Mar. Pollut. Bull.*, *32*, 599-608.

Geyer, W. R. "Final Report: Particle Trapping in the Lower Hudson Estuary," Hudson River Foundation, 1995.

U.S.EPA "Technical basis for deriving sediment quality criteria for nonionic organic contaminants for the protection of benthic organisms by using equilibrium partitioning," U.S. EPA Office of Water, 1993.

Chen, H.-W. *Fluxes of Organic Pollutants from Sediments in Boston Harbor*; Massachusetts Institute of Technology: Cambridge, MA, 1993, pp 145.

Baker, J. E.; Eisenreich, S. J.; Eadie, B. J. 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorinated biphenyl congeners in Lake Superior. *Environ. Sci. Technol.*, *25*, 500-509.

Baker, J. E.; Eisenreich, S. J. 1989. PCBs and PAHs as tracers of particulate dynamics in large lakes. *J. Great Lakes Res.*, *15*, 84-103.

Hirschberg, D.; Bokuniewicz, H. J. "Measurements of water temperature, salinity and suspended sediment concentrations along the axis of the Hudson River estuary 1980-1981," Marine Sciences Research Center, State University of New York, Stony Brook, 1981.

Karickhoff, S. W.; Brown, D. S.; Scott, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, *13*, 241-248.

Wu, S.-C.; Gschwend, P. M. 1988. Numerical modeling of sorption kinetics of organic compounds to soil and sediment particles. *Water Resour. Res.*, *8*, 1373-1383.

Wu, S.-C.; Gschwend, P. M. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.*, *20*, 717-725.